

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C04B 24/38, 24/04, 24/06, 24/10, 24/12, 24/08	A1	(11) International Publication Number: WO 97/27152 (43) International Publication Date: 31 July 1997 (31.07.97)
(21) International Application Number: PCT/US97/01110 (22) International Filing Date: 24 January 1997 (24.01.97) (30) Priority Data: 08/592,701 26 January 1996 (26.01.96) US (71) Applicant: THE NUTRASWEET COMPANY [US/US]; 1751 Lake Cook Road, Deerfield, IL 60015 (US). (72) Inventors: SKAGGS, Bryan; 11390 Turtleback Lane, San Diego, CA 92127 (US). RAKITSKY, Walter; 7271 Enders Avenue, San Diego, CA 92122 (US). SWAZEY, John; 2013 Oliver Avenue, San Diego, CA 92109 (US). DIAL, Harold; 11640 Avenida Marcella, San Diego, CA 92122 (US). (74) Agents: SIECKMANN, Gordon, F. et al.; Fitzpatrick, Cella, Harper & Scinto, 277 Park Avenue, New York, NY 10172-0194 (US).		(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: SUGAR AND/OR ACID ADDITION TO ANIONIC POLYSACCHARIDE-CONTAINING CEMENTITIOUS FORMULATIONS (57) Abstract In accordance with the present invention, it has been discovered that the rheological properties of a variety of anionic polysaccharide-containing cementitious systems can be improved by incorporating relatively small amounts of an organic sugar and/or an organic acid into the formulation. Sugar and/or acid addition to anionic polysaccharide-containing cementitious systems provides enhanced rheological control in a variety of cementitious systems. In particular, the introduction of sugar and/or acid to anionic polysaccharide-containing cementitious systems enhances its apparent viscosity.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

SUGAR AND/OR ACID ADDITION TO ANIONIC POLYSACCHARIDE-CONTAINING CEMENTITIOUS FORMULATIONS**FIELD OF THE INVENTION**

The present invention relates to novel anionic polysaccharide-containing cementitious systems having improved rheological properties, as well as methods for
5 improving the rheological properties of prior art anionic polysaccharide-containing cementitious systems.

BACKGROUND OF THE INVENTION

The majority of buildings are constructed with cementitious materials or systems that vary widely in
10 composition, design, and end use. As used herein, the term "cementitious system" refers to materials which, when mixed with an aqueous medium, bind, or impart an adhesive or cohesive behavior. Some examples include portland cements that are produced by burning limestone and clay, natural
15 and artificial pozzolanic cements (pozzolanic materials react with lime to form calcium silicate hydrates), slag cements, combinations of portland cement and granulated blast furnace slag, refractory cements (e.g., rapid set cements containing primarily calcium aluminate compounds,
20 such as, for example, Ciment Fondu produced by Lafarge, and Luminite, produced by Lehigh Cement Company), gypsum and desulfurized gypsum cements, expanding cements, fly ash, and the like. See, for example, Bye, G.C., "Portland Cement, Composition, Production and Properties", Pergamon
25 Press, New York, London, Ontario, Paris, Oxford (1983); Smith, Dwight K., "Cementing", Monograph Volume 4, Published by The Society of Petroleum Engineers, New York and Richardson, TX (1987).

Fresh cement or concrete paste is comprised of a
30 wide range of materials such as portland cement, fly ash,

silica fume, sand, aggregate, i.e., small rocks and water. Mixing, transporting, and placing the fresh concrete presents a number of challenges as the paste must remain highly fluid and ideally should provide homogenous transport of all particles. This problem is compounded because excessive water is frequently added to the mixture in efforts to enhance flow. The hydration of portland cement, for example, typically requires some 25-28 percent water basis weight of cement (BWOW). Unfortunately, excessive water can lead to a number of problems, such as, for example, bleed, sedimentation, reduced strength and durability, and poor bonding to structural reinforcement members.

Two types of materials can be used in admixture with cementitious formulations to enhance fresh paste flow, without the need to employ additional water, i.e., water reducers and superplasticizers. However, admixtures containing either material can induce excessive bleed and sedimentation. As used herein "bleed" refers to free water collection on the surface, while "sedimentation" refers to the segregation of particle size whether during placement, or static. Excessive bleed reduces durability and strength of the desired bond. In some cases, bleed water channels form on horizontal structural components, thereby reducing bond strength and creating corrosion sites. Aggregate segregation reduces the surface wear properties causing increased maintenance costs.

Recent technologies have provided a new class of cement additives, the so called rheological modifiers, or viscosity modifying agents (VMA). This class of additives comprises generally water-soluble polymers which function by increasing the apparent viscosity of the mix water. This enhanced viscosity facilitates uniform flow of the particles and reduces bleed, or free water formation, on the fresh paste surface. Underwater concrete placement

designs frequently require a polymer admixture to reduce fines loss during placement (Khayat, Kamal Henri, "Effects of Antiwashout Admixtures on Fresh Concrete Properties", Published in the ACI Structural Journal, Title No. 92-M18, 5 March-April, (1995)). Unfortunately, this also increases the resistance of the fresh cement paste to flow and may induce excessive frictional pressure during conveyment.

Accordingly, there is still a need in the art for methods to treat the above-described problems of bleed, 10 sedimentation, flow resistance, etc, encountered with existing cementitious formulations.

BRIEF DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has been discovered that the rheological properties of a 15 variety of anionic polysaccharide-containing cementitious systems can be improved by incorporating relatively small amounts of an organic sugar and/or an organic acid into the cementitious formulation.

Sugar and/or acid addition to anionic 20 polysaccharide-containing cementitious systems provides enhanced rheological control in a variety of cementitious systems. In addition, the introduction of sugar and/or acid to anionic polysaccharide-containing cementitious systems provides a number of advantages relative to prior 25 art systems, including enhanced rheological performance, improved water retention, enhanced durability, improved free water and sedimentation control, as well as reduced fines loss during underwater placement. The addition of sugar and/or acid to anionic polysaccharide-containing 30 cementitious systems enhances the stability of highly diluted microfine cementitious systems, and enhances the flow and workability of superworkable and self-leveling pastes. The homogenous set cement resulting from the

invention treatment of cementitious systems promotes bond strength and eliminates the need for vibrated concrete. Efficient free or bleed water control eliminates unsightly vugs or voids adjacent to the form work and thus enhances the appearance of the finished concrete. The invention methods provide additional benefits as well, such as, for example, enhanced color delivery in pigmented concrete and stabilized bubble entrapment in so called foamed or cellular cement systems. When used for treatment of sprayable cementitious systems, the invention method reduces rebound and sag.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, there are provided methods to improve the apparent viscosity of anionic polysaccharide-containing cementitious formulations. The invention method comprises adding to the cementitious formulation a viscosity enhancing amount of at least one viscosity enhancing additive selected from organic sugars having at least 6 carbon atoms, organic acids having at least 6 carbon atoms, or mixtures of any two or more thereof.

Cementitious formulations contemplated for use in the practice of the present invention include portland cements, pozzolanic cements, blast furnace slag cements, slag cements, masonry cements, construction cements, oil well cements, aluminous cements, expansive cements, air entrained cements, superworkable cements, microfine cements, colloidal cements, as well as so called "mud to cement" systems, whereby a drilling mud is converted into a cementitious material during the completion process of certain subterranean wellbores, and the like.

Organic sugars contemplated for use in the practice of the present invention typically have in the

range of 6 up to 50 carbon atoms. Preferably, sugars employed in the practice of the present invention are monosaccharides, disaccharides, trisaccharides, or a mixture of any two or more thereof.

5 Examples of sugars suitable for use in the practice of the present invention include glucose, gulose, idose, fructose, mannose, galactose, talose, allose, altrose, sucrose, maltose, lactose, melibiose, raffinose, gentianose, cellobiose, dextrose, mannitol, sorbitol, and
10 the like, as well as derivatives thereof (such as, for example, esters (e.g., sucrose octaacetate), aldose derivatives, glucosides (e.g., methyl glucoside), aldehydes, ketones, ethers (e.g., sucrose octabenzyl ether), acetals (e.g., O-benzylidenesucrose hexaacetate),
15 epoxides (e.g., D-glucopyranosyl-3,4-anhydro-B-D-ribohexulofuranoside hexaacetate), nitrogen derivatives, deoxy derivatives, and the like), and mixtures of any two or more thereof.

When sugars are used as the viscosity enhancing
20 additive contemplated by the invention method, the viscosity enhancing amount of sugar employed will typically fall in the range of 0.001 up to 1 wt %, based on the weight of the dry formulation. Presently preferred amounts of sugar contemplated for use in the practice of the
25 present invention fall in the range of about 0.05 up to 0.5 wt %. Amounts of added sugar substantially above about 0.5 wt % are generally to be avoided because it is at such levels that sugars begin to act as retarders of cement cure in typical cementitious formulations (although those of
30 skill in the art recognize that the dual functional properties of these additives may at times be desirable, depending on the contemplated application).

Organic acids contemplated for use in the practice of the present invention typically have in the

range of about 6 up to 36 carbon atoms. Those of skill in the art recognize that a variety of organic acids exist, e.g., optionally substituted saturated, mono-unsaturated or poly-unsaturated mono- or poly-carboxylic acids, optionally substituted arylcarboxylic acids, organosulfonic acids, organophosphonic acids, and the like. As employed herein, reference to "substituted" compounds embraces compounds bearing one or more substituents such as hydroxy, alkoxy (of a lower alkyl group, wherein "lower alkyl" refers to straight or branched chain alkyl radicals having in the range of about 1 up to 4 carbon atoms), mercapto (of a lower alkyl group), aryl, heterocyclic, halogen, trifluoromethyl, cyano, nitro, amino, carboxyl, carbamate, sulfonyl, sulfonamide, and the like.

Examples of carboxylic acids suitable for use in the practice of the present invention include caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, cyclohexanecarboxylic acid, phenylacetic acid, benzoic acid, α -naphthoic acid, β -naphthoic acid, ortho-toluic acid, meta-toluic acid, para-toluic acid, ortho-chlorobenzoic acid, meta-chlorobenzoic acid, para-chlorobenzoic acid, ortho-bromobenzoic acid, meta-bromobenzoic acid, para-bromobenzoic acid, ortho-nitrobenzoic acid, meta-nitrobenzoic acid, para-nitrobenzoic acid, cinnamic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid, salicylic acid, para-hydroxybenzoic acid, ascorbic acid, citric acid, sorbic acid, anthranilic acid, meta-aminobenzoic acid, para-aminobenzoic acid, ortho-methoxybenzoic acid, meta-methoxybenzoic acid, para-methoxybenzoic acid, and the like.

Organosulfonic acids suitable for use in the practice of the present invention typically have the

structure $R-S(O)_2-OH$, wherein R is selected from alkyl, substituted alkyl, aryl, substituted aryl, alkaryl, substituted alkaryl, aralkyl, substituted aralkyl, and the like. Examples include benzenesulfonic acid, 5 *p*-toluenesulfonic acid, *m*-nitrobenzenesulfonic acid, 3,4-dimethylbenzenesulfonic acid, and the like.

Organophosphonic acids suitable for use in the practice of the present invention typically have the structure $R-P(O)(OH)_2$, wherein R is selected from alkyl, 10 substituted alkyl, aryl, substituted aryl, alkaryl, substituted alkaryl, aralkyl, substituted aralkyl, and the like. Examples include phenylphosphonic acid, methylphosphonic acid, and the like.

When organic acids are used as the viscosity 15 enhancing additive contemplated by the invention method, the viscosity enhancing amount of acid employed will typically fall in the range of 0.001 up to 1 wt %, based on the weight of the dry formulation. Presently preferred amounts of organic acid contemplated for use in the 20 practice of the present invention fall in the range of about 0.05 up to 0.5 wt %.

Anionic polysaccharides contemplated for use in the practice of the present invention include xanthan gum, welan gum, gellan gum, rhamsan gum, S-657, carboxylated 25 cellulose ethers (CMC), and the like. The presently preferred anionic polysaccharide for use in the practice of the present invention is welan gum.

Welan gum (also referred to as S-130) is described in detail in U.S. Patent No. 4,342,866, the 30 entire contents of which are hereby incorporated by reference herein. Welan gum is a microbial polysaccharide produced under carefully controlled aerobic fermentation conditions by the organism *Alcaligenes* ATCC 31555. The

primary structure comprises a linear tetrasaccharide repeat unit of D-glucose, D-glucuronic acid, D-glucose and L-rhamnose. Welan gum has a backbone repeat unit with a single side substituent. The side sugar can be either
5 L-rhamnose or L-mannose. The molecular weight is estimated to be around 2 million. In solution, welan appears to exist as a double helix that builds viscosity through direct helical interaction via hydrogen bonding or through ion mediated association of helices. Intermolecular
10 hydrogen bonding between the main chain and side chains contribute to the stiff conformation of the molecule. This structure produces a molecule with excellent heat stability, extremely high viscosity at low shear rates, and salt tolerance in high pH calcium environments. Because of
15 its lack of hydrophobic substituents, welan gum has little activity at the air-water interface and generally does not cause foaming problems.

S-657 is described in detail in U.S. Patent No. 5,175,278, the entire contents of which are hereby
20 incorporated by reference herein. S-657 is a microbial polysaccharide produced under carefully controlled aerobic fermentation conditions by the organism *Xanthomonas* ATCC 53159. The primary structure comprises a linear tetrasaccharide repeat unit of D-glucose, D-glucuronic
25 acid, D-glucose and L-rhamnose. This repeat unit has a side chain composed of two rhamnose substituents linked through O-3 on the backbone 4-linked glucose residue (Moorhouse, Ralph, Structure/Property relationships of a Family of Microbial Polysaccharides, Industrial
30 Polysaccharides: Genetic Engineering, Structure/Property Relations and Applications, Elsevier Science Publishers B.V., Amsterdam (1987)). In contrast, welan gum (S-130), has the same backbone repeat unit with a single side substituent. The side sugar can be either L-rhamnose or
35 L-mannose.

Gellan gums and rhamsan gums have been well characterized in the art and are well known to those of skill in the art. See, for example, Campana et al., in Carbohydrate Research 231:31-38 (1992), and Moorhouse,
5 supra.

Carboxylated cellulose ethers have also been well characterized in the art and are well known to those of skill in the art. See, for example, Industrial Gums, Polysaccharides and Their Derivatives, Third Edition,
10 Whistler and BeMiller, eds. (Academic Press, 1993).

In accordance with another embodiment of the present invention, there are provided methods to improve the performance of anionic polysaccharides in cementitious formulations, said method comprising adding to said
15 formulation a performance enhancing amount of at least one performance enhancing additive selected from organic sugars having at least 6 carbon atoms, organic acids having at least 6 carbon atoms, or mixtures of any two or more thereof.

20 Organic sugars and organic acids contemplated for use in this aspect of the invention are as described above. Performance enhancing amounts of said performance enhancing additives typically fall in the range of 0.001 up to 1 wt %, based on the weight of the dry formulation.
25 Presently preferred amounts of organic sugars and/or organic acids contemplated for use in the practice of the present invention fall in the range of about 0.05 up to 0.5 wt %.

In accordance with yet another embodiment of the
30 present invention, there are provided anionic polysaccharide-containing cement formulations comprising:
cement,
anionic polysaccharide,

dispersant, and
a viscosity enhancing amount of at least one
viscosity enhancing additive selected from organic sugars
having at least 6 carbon atoms, organic acids having at
5 least 6 carbon atoms, or mixtures of any two or more
thereof.

Dispersants contemplated for use in the practice
of the present invention are typically either water
reducers or superplasticizers. As used herein, the term
10 "water reducer" means an agent, which in admixture with the
cementitious formulation, is capable of reducing mix water
concentration between 10 and 15% while maintaining
flowability of the same system with no added water reducer.
Water reducers contemplated for use in the practice of the
15 present invention include calcium, sodium or ammonium salts
of lignosulfonic acids, hydrocarbylcarboxylic acids,
organosulfonic acids, organophosphonic acids, mineral
acids, and the like.

As used herein, the term superplasticizer (which
20 is sometimes synonymous with "high range water reducer"
(HRWR), or in the case of oil well applications may be
referred to as a "dispersant") differs from normal water
reducers as they are capable of reducing water contents up
to 30% while providing similar flow behavior.

25 Superplasticizers have found a number of uses,
such as, for example, to impart improved workability, to
impart ease of conveyance, to enable the use of reduced
water content in fresh paste (thereby providing increased
durability). Superplasticizers are broadly classified into
30 four groups, i.e., sulfonated naphthalene-formaldehyde
condensate (SNF; these compounds are manufactured by a
number of companies including, but not limited to, Handy
Chemical (Disal), Boremco (Borem), Rohm and Haas (Tamol),
and Henkel (Lomar)); sulfonated melamine formaldehyde

condensate (SMF; e.g., compounds manufactured by SKW (Melment) and Handy Chemical (Meladyne)); modified lignosulfonates (MLS; which are commercially available from a number of companies including Georgia Pacific (LIGNOSITE), Borregaard (Vanisperse CB), and Chem-Lig (CA-37)); as well as other high molecular weight esters, such as, for example, sulfonic acid esters, carbohydrate esters, and the like. See, for example, Ramachandran, V.S., "Concrete Admixture Handbook", Properties Science, and Technology, Noyes Publications, Park Ridge, New Jersey, (1984); Kosmatka, Stephan H. and Panarese, William C., "Design and Control of Concrete Mixtures", Thirteenth Edition, Portland Cement Association, 5420 Old Orchard Road, Skokie, OL, (1994).

Organic sugars and organic acids contemplated for use in this aspect of the invention are as described above. The viscosity enhancing amount of sugar and/or acid employed in the practice of this aspect of the present invention will typically fall in the range of 0.05 up to 5 wt %, based on the dry weight of the total formulation. Presently preferred amounts of organic sugars and/or organic acids contemplated for use in the practice of this aspect of the present invention fall in the range of about 0.05 up to 0.5 wt %.

In accordance with still another embodiment of the present invention, there are provided modified anionic polysaccharides containing at least one property enhancing additive selected from organic sugars having at least 6 carbon atoms, organic acids having at least 6 carbon atoms, or mixtures of any two or more thereof, wherein the weight ratio of anionic polysaccharide to property enhancing additive falls in the range of about 1:10 up to 10:1. Presently preferred ratios of anionic polysaccharide to property enhancing additive fall in the range of about 1:5 up to 5:1.

The invention will now be described in greater detail with reference to the following non-limiting examples.

Example 1

5 It has surprisingly been observed that rheological test results for different welan-containing cements can vary widely for different portland cements, as demonstrated by the data presented in Table 1. The cement test data are presented as Fann dial reading (FDR), and
10 obtained using a Fann 35 (R1, B1, F0.2) rotating at 100 rpm.

Thus, type I/II cements are mixed using 400 grams of cement, 0.4 grams of welan gum (0.1 wt %), 4.0 grams of polynaphthalene sulfonate superplasticizer (1 wt %).
15 Cement and water (400 grams) are premixed for three minutes, superplasticizer and gum are dry blended together and added. Once superplasticizer and gum are added, the slurry is mixed an additional 10 minutes.

Table 1

CEMENT ¹	A	B	C	D	E	F
Cement test (FDR)	81	77	63	60	54	43

¹ Six different Portland cement samples as obtained from several different finished grinding plants were employed

To determine the effect of various additives on the performance of type I/II portland cement containing welan gum, cement (400 grams), 0.1 wt % additive (i.e., organic sugar or organic acid as described hereinabove),
5 and 0.1 wt % welan (4 grams) were dry blended with 1 wt % superplasticizer. The dry blend was then added to the mix

water and sampled after 3 and 10 minutes mix time. Results are summarized in Table 2.

Table 2

5	SAMPLE	FDR @ 3 min	FDR @ 10 min
	Control	34	38
	Ascorbic acid	47	56
	Dextrose	39	44
	Citric acid	42	48
10	Mannitol	44	49
	Sorbitol	40	43
	Sorbic acid	36	43

Compared to the control sample, the sample containing ascorbic acid exhibited a 38% increase in viscosity in 3 minutes mix time (with an even more dramatic increase of 47% after 10 minutes mix time). Similarly, the welan
 5 sample mixed with mannitol exhibited a substantial increase in viscosity at both 3 minutes mix time (29%) and 10 minutes mix time (24%).

Example 2

Performance in Oil Well Cements

10 Proper cementitious technique and job design provide the key to efficient oil well completion. A proper cement job forms a hydraulic seal with the subterranean formation thus preventing reservoir fluids from entering the annulus and migrating to a lower pressure zone, or in
 15 extreme cases, all of the way to the surface. A less than ideal cement job may allow loss of hydrocarbons and in extreme cases, can lead to oil well fires. Once a steel pipe is lowered into the well bore, cement is pumped down this pipe, or so called casing. The cement slurry is
 20 displaced up the formation casing annulus. Once in place,

the slurry must effectively transmit sufficient hydrostatic pressure to prevent formation fluids from entering the well bore until the cement has sufficient strength to prevent fluid migration.

5 Efficient slurry placement requires rheological manipulation to provide a highly fluid cement slurry with minimal frictional pressure during placement. In addition, the cement slurry must resist water, or so called fluid loss, to the surrounding formation both during placement
10 and in the static state. Once placed, this same slurry rheology must prevent particle sedimentation and free water formation. Slurries developing excessive frictional pressure during placement may cause premature job shutdown, or fracture of formation, either situation is highly
15 undesirable. Should a cement slurry lose excessive water during placement, the particles may bridge and disrupt flow. After placement, fluid loss concentrates cement particles and can form particle bridges. Either condition may cause excessive hydrostatic pressure decay and lead to
20 fluid migration.

Combinations of mannitol and welan were compared in class G oil well cement slurries mixed according to API Specification 10:

Table 3

Welan gum performance (Free water v. Viscosity)
in 1.25 water:Class G oil well cement slurry

Test ¹	% Welan ²	% Dispersant ³	% Mannitol ²	Mix time (mins.)	FDR 100 rpm	24 hr. % Free Water
1	0.1	0.5	0.1	3 10	30 30	0
2	0.075	0.25	0.125	3 10	24 24	5
3	0.075	0.75	0.075	3 10	20 26	9
4	0.125	0.25	0.125	3 10	39 38	0
5	0.125	0.25	0.075	3 10	39 35	4
6	0.075	0.25	0.075	3 10	23 22	20
7	0.125	0.75	0.125	3 10	40 46	0
8	0.075	0.75	0.125	3 10	22 26	1.4
9	0.125	0.75	0.075	3 10	36 43	4

¹ Each test employed 320 grams of Class G cement (Boren 600HSP basis weight cement), and 400 grams of tap water

² Welan and Mannitol basis weight water

³ The dispersant employed is a sulfonated naphthalene formaldehyde condensate

A control grout containing 0.5 wt % dispersant and 0.1 wt % welan gum developed 26 % free water. In contrast, each of the tests summarized in Table 3 produce substantially reduced levels of free water, relative to the control. Indeed, three of the tests described above produced zero free water (i.e., Test 1, wherein 0.1 wt % mannitol, 0.1 wt % welan gum and 0.5 wt % dispersant are employed; Test 4, wherein 0.125 wt % mannitol, 0.125 wt % welan gum and 0.25 wt % dispersant are employed; and Test 7, wherein 0.125 wt % mannitol, 0.125 wt % welan gum and 0.75 wt % dispersant are employed).

The results presented herein demonstrate that the performance of anionic polysaccharides such as welan gum can be significantly enhanced by the addition of organic sugars and/or acids.

While the invention has been described in detail with reference to certain preferred embodiments thereof, it will be understood that modifications and variations are within the spirit and scope of that which is described and claimed.

CLAIMS

That which is claimed is:

1. A method to improve the apparent viscosity of anionic polysaccharide-containing cementitious formulations, said method comprising adding to said formulation a viscosity enhancing amount of at least one
5 viscosity enhancing additive selected from organic sugars having at least 6 carbon atoms, organic acids having at least 6 carbon atoms, or mixtures of any two or more thereof.
2. A method according to claim 1 wherein said cementitious formulation is selected from portland cement, pozzolanic cement, blast furnace slag cement, slag cement, masonry cement, construction cement, oil well cement,
5 aluminous cement, expansive cement, air entrained cement, superworkable cement, microfine cement or colloidal cement, a mud to cement system, or mixtures of any two or more thereof.
3. A method according to claim 1 wherein said sugar has in the range of 6 up to 50 carbon atoms.
4. A method according to claim 3 wherein said sugar is a monosaccharide, a disaccharide, a trisaccharide, or a mixture of any two or more thereof.
5. A method according to claim 4 wherein said sugar is selected from glucose, gulose, idose, fructose, mannose, galactose, talose, allose, altrose, sucrose, maltose, lactose, melibiose, raffinose, gentianose,
5 cellobiose, dextrose, mannitol, sorbitol, or derivatives thereof, or mixtures of any two or more thereof.

6. A method according to claim 1 wherein the viscosity enhancing amount of sugar falls in the range of 0.001 up to 1 wt %, based on the weight of the dry formulation.

7. A method according to claim 1 wherein said organic acid has in the range of about 6 up to 36 carbon atoms.

8. A method according to claim 7 wherein said organic acid is an optionally substituted saturated, mono-unsaturated or poly-unsaturated mono- or poly-carboxylic acid, an optionally substituted arylcarboxylic acid,
5 organosulfonic acid or organophosphonic acid.

9. A method according to claim 7 wherein said organic acid is selected from caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid,
5 cyclohexanecarboxylic acid, phenylacetic acid, benzoic acid, α -naphthoic acid, β -naphthoic acid, ortho-toluic acid, meta-toluic acid, para-toluic acid, ortho-chlorobenzoic acid, meta-chlorobenzoic acid, para-chlorobenzoic acid, ortho-bromobenzoic acid, meta-bromobenzoic acid, para-bromobenzoic acid, ortho-nitrobenzoic acid, meta-nitrobenzoic acid, para-nitrobenzoic acid, cinnamic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid, salicylic acid,
10 para-hydroxybenzoic acid, ascorbic acid, citric acid, sorbic acid, anthranilic acid, meta-aminobenzoic acid, para-aminobenzoic acid, ortho-methoxybenzoic acid, meta-methoxybenzoic acid or para-methoxybenzoic acid.

10. A method according to claim 7 wherein the viscosity enhancing amount of acid falls in the range of 0.001 up to 1 wt %, based on the weight of the dry formulation.

11. A method according to claim 1 wherein said anionic polysaccharide is selected from welan gum, gellan gum, rhamsan gum, S-657 or carboxylated cellulose ethers.

12. A method according to claim 1 wherein said anionic polysaccharide is welan gum.

13. A method to improve the performance of anionic polysaccharides in cementitious formulations, said method comprising adding to said formulation a performance enhancing amount of at least one performance enhancing
5 additive selected from organic sugars having at least 6 carbon atoms, organic acids having at least 6 carbon atoms, or mixtures of any two or more thereof.

14. An anionic polysaccharide-containing cement formulation comprising:

cement,
anionic polysaccharide,
5 dispersant, and

a viscosity enhancing amount of at least one viscosity enhancing additive selected from organic sugars having at least 6 carbon atoms, organic acids having at least 6 carbon atoms, or mixtures of any two or more
10 thereof.

15. An anionic polysaccharide-containing cement formulation according to claim 14 wherein said anionic polysaccharide is selected from welan gum, gellan gum, rhamsan gum, S-657 or carboxylated cellulose ethers.

16. An anionic polysaccharide-containing cement formulation according to claim 14 wherein said anionic polysaccharide is welan gum.

17. An anionic polysaccharide-containing cement formulation according to claim 14 wherein said cement is selected from portland cement, pozzolanic cement, blast furnace slag cement, slag cement, masonry cement, construction cement, oil well cement, aluminous cement, expansive cement, air entrained cement, superworkable cement, microfine cement or colloidal cement, a mud to cement system, or mixtures of any two or more thereof.

18. An anionic polysaccharide-containing cement formulation according to claim 14 wherein said dispersant is a water reducer or a superplasticizer.

19. An anionic polysaccharide-containing cement formulation according to claim 17 wherein said water reducer is selected from calcium, sodium or ammonium salts of lignosulfonic acids, hydrocarbylcarboxylic acids, organosulfonic acids or organophosphonic acids.

20. An anionic polysaccharide-containing cement formulation according to claim 18 wherein said superplasticizer is selected from sulfonated naphthalene-formaldehyde condensate, sulfonated melamine formaldehyde condensate, modified lignosulfonates, as well as other high molecular weight esters.

21. An anionic polysaccharide-containing cement formulation according to claim 14 wherein said sugar has in the range of 6 up to 50 carbon atoms.

22. An anionic polysaccharide-containing cement formulation according to claim 21 wherein said sugar is a monosaccharide, a disaccharide, a trisaccharide, or a mixture of any two or more thereof.

23. An anionic polysaccharide-containing cement formulation according to claim 22 wherein said sugar is selected from glucose, gulose, idose, fructose, mannose, galactose, talose, allose, altrose, sucrose, maltose, 5 lactose, melibiose, raffinose, gentianose, cellobiose, dextrose, mannitol or sorbitol.

24. An anionic polysaccharide-containing cement formulation according to claim 14 wherein the viscosity enhancing amount of sugar falls in the range of 0.05 up to 5 wt %, based on the weight of the cement component.

25. An anionic polysaccharide-containing cement formulation according to claim 14 wherein said organic acid has in the range of about 6 up to 36 carbon atoms.

26. An anionic polysaccharide-containing cement formulation according to claim 25 wherein said organic acid is an optionally substituted saturated, mono-unsaturated or poly-unsaturated mono- or poly-carboxylic acid, an 5 optionally substituted arylcarboxylic acid, an organosulfonic acid or an organophosphonic acid.

27. An anionic polysaccharide-containing cement formulation according to claim 25 wherein said organic acid is selected from caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, 5 oleic acid, linoleic acid, linolenic acid, cyclohexanecarboxylic acid, phenylacetic acid, benzoic acid, α -naphthoic acid, β -naphthoic acid, ortho-toluic acid, meta-toluic acid, para-toluic acid, ortho-chlorobenzoic acid, meta-chlorobenzoic acid, para-10 chlorobenzoic acid, ortho-bromobenzoic acid, meta-bromobenzoic acid, para-bromobenzoic acid, ortho-nitrobenzoic acid, meta-nitrobenzoic acid, para-nitrobenzoic acid, cinnamic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic 15 acid, isophthalic acid, terephthalic acid, salicylic acid, para-hydroxybenzoic acid, ascorbic acid, citric acid, sorbic acid, anthranilic acid, meta-aminobenzoic acid, para-aminobenzoic acid, ortho-methoxybenzoic acid, meta-methoxybenzoic acid or para-methoxybenzoic acid.

28. An anionic polysaccharide-containing cement formulation according to claim 14 wherein the viscosity enhancing amount of acid falls in the range of 0.05 up to 5 wt %, based on the weight of the cement component.

29. A modified anionic polysaccharide containing at least one property enhancing additive selected from organic sugars having at least 6 carbon atoms, organic acids having at least 6 carbon atoms, or mixtures of any 5 two or more thereof, wherein the weight ratio of anionic polysaccharide to property enhancing additive falls in the range of about 1:10 up to 10:1.

30. A modified anionic polysaccharide according to claim 29 wherein said sugar has in the range of 6 up to 50 carbon atoms.

31. A modified anionic polysaccharide according to claim 30 wherein said sugar is a monosaccharide, a disaccharide, a trisaccharide, or a mixture of any two or more thereof.

32. A modified anionic polysaccharide according to claim 31 wherein said sugar is selected from glucose, gulose, idose, fructose, mannose, galactose, talose, allose, altrose, sucrose, maltose, lactose, melibiose, 5 raffinose, gentianose, cellobiose, dextrose, mannitol or sorbitol.

33. A modified anionic polysaccharide according to claim 29 wherein said organic acid has in the range of about 6 up to 36 carbon atoms.

34. A modified anionic polysaccharide according to claim 31 wherein said organic acid is an optionally substituted saturated, mono-unsaturated or poly-unsaturated mono- or poly-carboxylic acid, an optionally substituted 5 arylcarboxylic acid, an organosulfonic acid or an organophosphonic acid.

35. A modified anionic polysaccharide according to claim 31 wherein said organic acid is selected from caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, 5 linoleic acid, linolenic acid, cyclohexanecarboxylic acid, phenylacetic acid, benzoic acid, α -naphthoic acid, β -naphthoic acid, ortho-toluic acid, meta-toluic acid, para-toluic acid, ortho-chlorobenzoic acid, meta-chlorobenzoic acid, para-chlorobenzoic acid, ortho-10 bromobenzoic acid, meta-bromobenzoic acid, para-bromobenzoic acid, ortho-nitrobenzoic acid, meta-nitrobenzoic acid, para-nitrobenzoic acid, cinnamic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic 15 acid, salicylic acid, para-hydroxybenzoic acid, ascorbic acid, citric acid, sorbic acid, anthranilic acid, meta-aminobenzoic acid, para-aminobenzoic acid, ortho-methoxybenzoic acid, meta-methoxybenzoic acid or para-methoxybenzoic acid.

36. A modified anionic polysaccharide according to claim 29 wherein said anionic polysaccharide is selected from welan gum, gellan gum, rhamsan gum, S-657 or carboxylated cellulose ethers.

37. A modified anionic polysaccharide according to claim 29 wherein said anionic polysaccharide is welan gum.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/01110

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B24/38 C04B24/04 C04B24/06 C04B24/10 C04B24/12
C04B24/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 080 812 A (HALLIBURTON CO) 10 February 1982 see page 1, line 52 - page 2, line 48 see page 2, line 64-65 see page 3, line 1-8 see page 5; tables 1,	13-15, 17,25-28
A	---	1,2, 7-12,29, 33,34
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

A document member of the same patent family

Date of the actual completion of the international search

29 April 1997

Date of mailing of the international search report

25. 06. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Mini, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/01110

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 405 306 A (GRACE W R & CO) 2 January 1991 see page 2, line 50 - page 3, line 5 see page 2, line 26-27 see page 5, line 6-8 see page 6; table I see claims 22-26	13-15, 17,25-28
A		1,2, 7-12,29, 33,34
Y	--- US 5 447 197 A (RAE PHILIP ET AL) 5 September 1995 see column 2, line 40-54 see column 4, line 10-21 see column 4, line 63 - column 5, line 2 see examples 1,9-11,26; table 1 see claims 1-3	13-28
Y	--- GB 1 068 886 A (MARTIN MARIETTA CORPORATION) 17 May 1967 see page 5; tables IV,V	13-28
Y	--- US 5 180 430 A (GARTNER ELLIS M ET AL) 19 January 1993 see column 2, line 38; claim 1	13-28
Y	--- EP 0 290 198 A (MERCK & CO INC) 9 November 1988 see page 2, line 20-23 see page 3, line 18-19 see page 5, line 39	13-28
A	--- DATABASE WPI Section Ch, Week 9436 Derwent Publications Ltd., London, GB; Class A93, AN 94-290731 XP002030451 & JP 06 219 807 A (SHINETSU CHEM IND CO LTD), 9 August 1994 see abstract	1-32
A	--- EP 0 507 419 A (MERCK & CO INC) 7 October 1992 see page 2, line 39-58 see page 3, line 20-32 see page 5, line 31 -----	13-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 97/01110

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2080812 A	10-02-82	AU 547062 B	03-10-85
		AU 7280081 A	23-09-82
		BR 8104405 A	30-03-82
		CA 1163090 A	06-03-84
		DE 3126489 A	27-05-82
		NL 8103326 A	01-02-82
		US 4455169 A	19-06-84

EP 0405306 A	02-01-91	AU 635277 B	18-03-93
		AU 5698790 A	03-01-91
		CA 1337360 A	17-10-95
		DE 69005373 D	03-02-94
		DE 69005373 T	14-04-94
		ES 2047762 T	01-03-94
		JP 3232751 A	16-10-91
		SG 31694 A	25-11-94
		US 5294256 A	15-03-94

US 5447197 A	05-09-95	EP 0741679 A	13-11-96
		NO 963103 A	19-09-96
		WO 9519942 A	27-07-95
		US 5547506 A	20-08-96

GB 1068886 A		BE 650865 A	22-01-65
		FR 1410267 A	15-12-65
		NL 6407904 A,B	28-10-65
		US 3432317 A	11-03-69

US 5180430 A	19-01-93	AU 649594 B	26-05-94
		AU 2608792 A	22-04-93
		CA 2079923 A	17-04-93
		GB 2260537 A,B	21-04-93
		JP 5213650 A	24-08-93
		NZ 244497 A	26-07-94
		ZA 9207505 A	26-09-94

EP 0290198 A	09-11-88	AU 602080 B	27-09-90
		AU 1566488 A	10-11-88
		CA 1322011 A	07-09-93
		CA 1324127 A	09-11-93

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/01110

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0290198 A		CN 1030224 A	11-01-89
		CN 1065259 A,B	14-10-92
		DE 3877411 A	25-02-93
		EP 0507419 A	07-10-92
		IE 62112 B	14-12-94
		JP 63315547 A	23-12-88
		KR 9601425 B	27-01-96
		US 4963668 A	16-10-90
		US 5004506 A	02-04-91

EP 0507419 A	07-10-92	AU 602080 B	27-09-90
		AU 1566488 A	10-11-88
		CA 1322011 A	07-09-93
		CA 1324127 A	09-11-93
		CN 1030224 A	11-01-89
		CN 1065259 A,B	14-10-92
		DE 3877411 A	25-02-93
		EP 0290198 A	09-11-88
		IE 62112 B	14-12-94
		JP 63315547 A	23-12-88
		KR 9601425 B	27-01-96
		US 4963668 A	16-10-90
		US 5004506 A	02-04-91
